

CHAPTER III



MATERIALS & METHODS

3.1 Materials

3.1.1 Synthetic samples

All samples were prepared by dissolving the contaminant in a buffer solution. The buffer solution was prepared by mixing 1.8 g monobasic sodium phosphate and 0.4 g dibasic sodium phosphate in 1 L deionized water. Initial concentrations of TCE were 10 ppm, 50 ppm and 100 ppm (see calculations in Appendix D).

3.1.2 Chemicals and reagents

Chemicals and reagents were sodium hydroxide, potassium hydroxide, nitric acid, sulfuric acid, hydrochloric acid, sodium thiosulfate, dibasic sodium phosphate, monobasic sodium phosphate, sodium bicarbonate, sodium persulfate, potassium oxalate, 1,10-phenanthroline, sodium propionate, ferric chloride, ferrous ammonium sulfate, ammonium thiocyanate, deionized water, and pentane. Persulfate solution was prepared by dissolving sodium persulfate in the phosphate buffer solution. The pH value of all solution was controlled by the phosphate buffer solution and adjusted with

0.1N sodium hydroxide and 0.1N nitric acid. The chemical reaction was stopped by sodium thiosulfate solution (see calculations in Appendix D).

3.2 Experimental set-up

3.2.1 Heat activated persulfate oxidation method

The heat activated persulfate oxidation system was made up of 50 mL crimp seal vials with aluminium seal and silicone Teflon septa, and a shaking water bath illustrated in Figure 3.1. A shaking water bath was used for temperature control and mixing. All experiments were done in triplicate. Control tests were conducted in parallel.



Figure 3.1 Heat activated persulfate oxidation system

3.2.2 UV activated persulfate oxidation method

The UV activated persulfate oxidation system consisted of 50 mL crimp seal vials with aluminium seal and silicone Teflon septa, and 2 UV lamps, illustrated in Figure 3.2, 3.3 and 3.4. Mixing was provided by a magnetic stirrer. The radiation sources were Phillips TUV 10W fluorescent lamps emitting between 253.7-578.0 nm, with a maximum centered at 253.7 nm. The average UV intensity was 10.96 μ Einstein/s (see UV intensity measurement in Appendix C). A paper box attached with aluminium foil, illustrated in Figure 3.5, covered the system for safety. The temperature was controlled at 25°C by fans. All tests were done in triplicate. Control tests for examining the behavior of each contaminant without the oxidant were carried out in parallel.

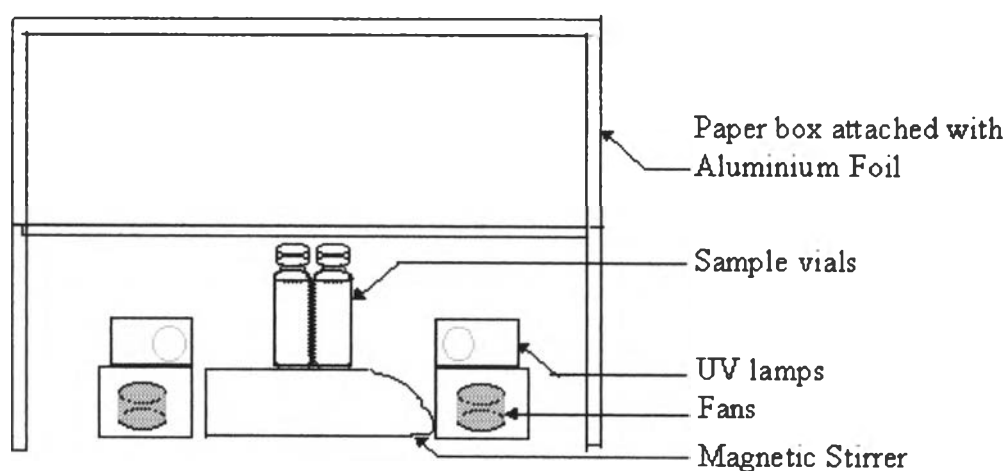


Figure 3.2 Diagram of UV activated persulfate oxidation system (front view)

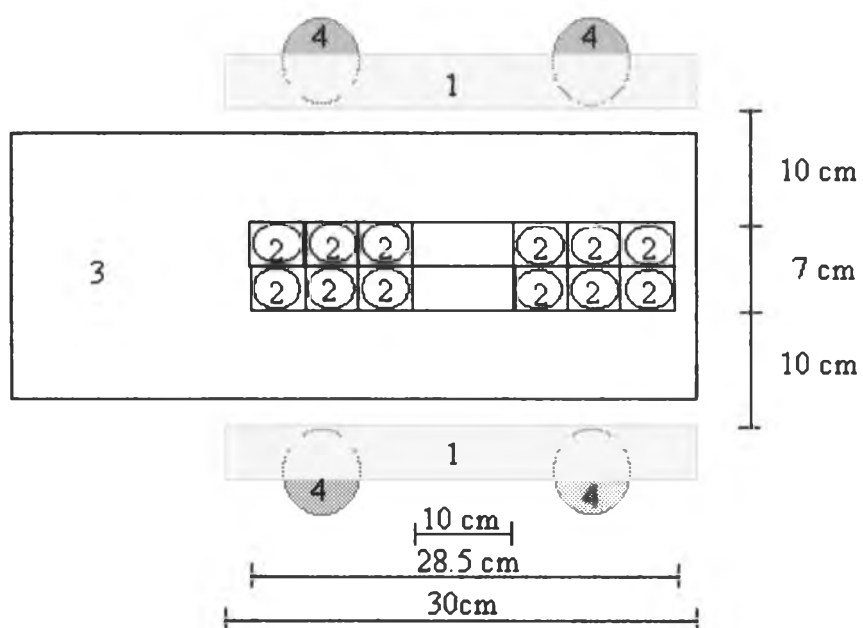


Figure 3.3 Diagram of UV activated persulfate oxidation system (top view)

(1=UV lamp, 2=Sample vial, 3=Magnetic stirrer, 4=fan)



Figure 3.4 UV activated persulfate oxidation system



Figure 3.5 UV activated persulfate oxidation system (covered system)

3.2.3 Persulfate oxidation method without heat and UV activated condition

The persulfate oxidation system without heat and UV activated condition consisted of the same equipments of heat activated persulfate oxidation except that the temperature was 25°C. All tests were done in triplicate

3.3 Experimental procedure

3.3.1 Heat activated persulfate oxidation method

All procedure was done in safety hood. Initial concentration of TCE solution was 10 ppm. The synthetic samples were added into 50 mL crimp seal vials in the

heat activated persulfate system at 40°C which was the optimum temperature of heat activated persulfate oxidation obtained from Liang et al. (2003)'s study. Then, the persulfate solution was distributed into the vials by a syringe. The vials were removed at different time for a kinetic evaluation. The pH of solutions was adjusted to 6.36. The molar ratios of persulfate and contaminant were 5:1,10:1 and 15:1 for each set of experiment. The optimal persulfate/TCE molar ratio of this system was selected from the molar ratios due to TCE removal percentage and rate constant. The heat activated persulfate oxidation method was tested at initial TCE concentrations of 50 ppm and 100 ppm at the optimal persulfate/TCE molar ratio.

3.3.2 UV activated persulfate oxidation method

The experimental procedure for the UV activated persulfate oxidation was the same as that for the heat activated persulfate oxidation except that the temperature was 25°C.

3.3.3 Persulfate oxidation method without heat and UV activated condition

The experimental procedure for the persulfate oxidation system without heat and UV activated condition was the same as that for the heat activated persulfate oxidation except that the temperature was 25°C, which is ambient temperature, and the initial concentration of TCE was only 10 ppm.

3.4 Analytical methods

3.4.1 Analysis of TCE

Analytical method of TCE was adapted from method 6232B of Standard Methods (Clesceri et al., 1998) using a gas chromatograph equipped with a linearized electron capture detector (a Hewlett-Packard 6890) and a HP-5 (5% Phenyl Methyl Siloxane) fused silica capillary column (30m x 0.32 mm ID; thickness, 0.25 μ m).

The operating conditions were injector temperature 250°C, detector temperature 250°C, initial column temperature 80°C, and programmed at 80°C to 100°C at a rate of 25°C/min, and 100°C to 150°C at a rate of 40°C/min, and 150°C to 300°C at a rate of 90°C/min then post column temperature 80°C and hold for 2 min. Helium was used as carrier gas with gas flow of 20 mL/min, and a 40:1 injector split ratio. The make up gas was nitrogen with gas flow of 20 mL/min. TCE has a retention time of 4.123. A solvent used for extracting of TCE was pentane.

3.4.2 Measurement of UV intensities

UV intensities were measured by ferrioxalate actinometer which was the most widely accepted standard actinometer (Kuhn et al., 2004) (see UV intensities of the UV activated persulfate oxidation system in Appendix C). The procedure was described in Kuhn et al. (2004) and Murov et al. (1993).

3.4.3 CO₂ analysis

CO₂ analysis was adapted from a procedure in Goffman et al. (2004) and OSHA Method ID-172 (OSHA,1990). pH of solution was decreased to less than 3 by adding 6 N HCL to convert different forms of inorganic carbon, such as bicarbonates, and soluble and insoluble carbonates to aqueous and gaseous CO₂. The gaseous CO₂ was determined with a gas chromatograph equipped with thermal conductivity detector. Standards were made by using accurate concentrations of sodium carbonate with the liquid/gas headspace volume ratios of samples and at pH 2. Total inorganic CO₂ concentrations of standards were calculated from mols of NaHCO₃ which equal mols of CO₂ at pH 2 (Goffman et al., 2004).

The operating conditions of GC/TCD were injector temperature 250°C, detector temperature 250°C, initial column temperature 60°C, and programmed at 60°C hold for 2 min, and 60°C to 240°C at a rate of 60°C/min, and hold at 240°C for 1 min. Helium was used as carrier gas with gas flow of 8.6 mL/min, and a injector splitless.

From the measurement, CO₂ cannot be analyzed by this procedure because the resolution of the peak of CO₂ was too low compared with other gases in the atmosphere, which have much more concentration (see chromatograms in Appendix A). The procedure was ineffective in this study and might be a result of using a

GC/TCD (OSHA Method ID-172) instead of an infra red gas analyzer (Goffman et al.,2004).

Although many analytical methods can be used for determination of CO₂, high concentration and high amount of gas need to be sacrificed for the analysis. OSHA Method ID-172 requires 2 to 5-L samples in a range of 500 to 30,000 ppm of CO₂. NMAM method 6603 (NIOSH, 1994) using 3.5- L samples in study for accuracy requires sample volume large enough to be precisely readable in a CO₂ concentration range of 500-15,000 ppm. The analytical methods were usable in this study because the maximum volume of CO₂ was only 7 mL with maximum CO₂ concentration of 47.9, 239.5, and 479 ppm for 10 ppm TCE, 50 ppm TCE, and 100 ppm TCE, respectively in a case that organic carbon of TCE was completely transform to gaseous CO₂.

3.4.4 Other by-products analysis

Other by-products were measured by a gas chromatography with mass spectrometry.

3.5.5 pH measurement

pH was measured using a pH meter (Sension™ model 51935-00)